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Characterization of particulate matter sources in an urban environment

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ABSTRACT

Daily time series measurements of elements or compounds are widely used to apportion the contribution of specific sources of particulate matter concentration in the atmosphere. We present results obtained for the urban area of Genoa (Italy) based on several hundred of PM10, PM2.5 and PM1 daily samples collected in sites with different geo-morphological and urbanization characteristics. Elemental concentrations of Na to Pb were obtained through Energy Dispersive X-Ray Fluorescence (ED-XRF), and the contributions of specific sources of particulate matter (PM) concentration were apportioned through Positive Matrix Factorization (PMF). By sampling at different sites we were able to obtain, in each PM fraction, the average and stable values for the tracers of specific sources, in particular traffic (Cu, Zn, Pb) and heavy oil combustion (V, Ni). We could also identify and quote the contamination of anthropogenic PM in "natural" sources (sea, soil dust). Sampling at several sites in the same urban area allowed us to resolve local characteristics as well as to quote average values.

1. Introduction

In recent years, atmospheric aerosols have been studied extensively (Charlson et al., 1992; Harrison et al., 2001; Satheesh and Moorthy, 2005). Their effects on human beings are well established and have legal ramifications. According to European Directive 1999/30/EC, the concentration of PM10 (PM10=atmospheric particulate matter with aerodynamic diameter, $D_{ae} \leq 10$ μm) in Europe is committed to reach an average annual value of less than 20 μg m^{-3} by 2010. Large datasets of PM10 concentration are collected daily for regulatory purpose in several countries (Manoli et al., 2004; Mantis et al., 2005) but information on fine fractions (PM1, for instance) and their composition is still poor. Recent works indicate that the finer fraction of PM is more dangerous for human health (Schwartz et al., 1996; Maynard and Howard, 1999; Wichmann and Peters, 2000; Samet 2000; Chow et al., 2002a,b; Stieb et al., 2002; Fernandez et al., 2003).

Up to now, PM concentrations have been routinely monitored. However, this level of monitoring is insufficient and a measurement of the elemental and chemical composition of PM is recommended in order to achieve a more complete picture. Indeed concentration limits have been set in Europe for some toxic elements (Pb, Ni, Cd, Hg; see the recent European Directive 2004/107/CE). Element and/or compound measurements can also help to trace specific emission patterns. Thus, the knowledge of the chemical composition of particulate matter can be used to evaluate the impacts of the various pollution sources on air quality. Several "source apportionment" strategies have been developed; receptor models (Gordon, 1988) are presently considered the most effective approach. These models usually provide three pieces of information: the number of (major) sources of particulate matter, the source profiles and the mass contribution of each source to total PM. These models single out groups of elements with correlated concentration trends, which

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are associated with real-world sources on the basis of source profile. Natural sources can usually be identified by constant concentration ratios among their constituents, for instance Na–Cl and Al–Si–Ti (sea-salt and soil dust respectively, (Chueinta et al., 2000)). Some anthropogenic sources also have clear tracers, like V–Ni, for heavy oil combustion (Hedberg et al., 2005). However these concentration ratios cannot be assumed constant at all sites. For instance, in the past, traffic emissions have been firmly identified due to the Br–Pb correlation, with an average Pb to Br concentration ratio of 3.0±0.2 (D'Alessandro et al., 2003). Since the ban of leaded fuel, traffic profiles have been based on tracers like Cu (from abrasion of asbestos-free brake linings (Salma and Maenhaut, 2006; Iijima et al., 2007) and from lubricating oil), Zn (from metallic brakes and, particularly in the PM10 fraction, from the rubber wear of tires) and Pb (still present in petrol). Element ratios reported in the literature vary greatly (Marcazzan et al., 2003; Yeung et al., 2003; Cyrys et al., 2003). Similarly, aerosols from different sources, can produce artefacts in receptor models, therefore the same tracer may be ascribed to multiple sources. Problems may also arise when several sources are aligned and driven together to the receptor site by the same wind pattern or when the source profiles are not constant with time. Even in the case of "natural sources", methods for disentangling true natural elements from contaminants originating from polluted areas may be necessary. Finally, PM samples are usually monitored on a daily basis, whereas (in particular in towns) a shorter time resolution (1–2 h) would be necessary to separate the rapidly changing sources related to urban life (Ogulei et al., 2005, 2006; Park et al., 2005, 2006; Zhou et al., 2005; Mazzei et al., 2006, 2007).

In this work, the receptor model known as Positive Matrix Factorization (PMF) (Paatero and Tapper, 1994) has been exploited: this model has been recently asserted as a very reliable tool at international level. PMF is a variant of factor analysis (Heidam, 1982; Thurston and Spengler, 1985), which constrains factor loading and factor score to non-negative values. The city of Genoa has been chosen as a "field laboratory": during three years, several sampling campaigns have been performed in various districts inside the urban area. A large set of PM10, PM2.5 and PM1 daily samples used to single out the major characteristics of local PM have been collected. Significant findings have extracted from this monitoring data and developed into a methodology that can be applied elsewhere.

2. Materials and methods

Genoa (44° 24′ 15″ N, 08° 54′ 15″ E), the most populated coastal town in the northwestern Italy (about 700,000 inhabitants), has developed around an important harbour and large steelworks in the western suburbs and is largely influenced by a Mediterranean climate. A chain of hills and mountains, up to 1000 m a.s.l., lies immediately behind the coastline, causing the development of a narrow 40 km long urban area along the sea. The peculiar topology produces a complex meteorological regime characterized by sudden changes in wind direction and speed. PM data, collected in the past by local authorities, show uncorrelated concentration trends in different parts of the city.

During the monitoring campaigns we used sequential PM samplers, most designed according to the CEN standard for PM10 collection and one according to the US EPA standards for PM10 and PM2.5. Equivalence within 10% between the EPA sampler and the CEN standard has been previously established (Chiari et al., 2005). The samplers were equipped with the appropriate inlets for the selection of the PM10, PM2.5 or PM1 fraction (PM with aerodynamic diameter smaller than 10, 2.5 and 1 μm, respectively) and were operated from May 2002 to July 2005. Our sampling devices were deployed in the urban area of Genoa, at different nodes of the municipal air quality network: "Brignole", "Cornigliano", "Multedo" and "C.so Firenze". In Table 1 we report a brief description of the sampling sites and periods, and the positions and distances are indicated in Fig. 1.

The PM concentration was determined using 47 mm Teflon membranes with 2 μm pore size (particle retention >99.7% with particle size of 0.3 μm, see http://www.whatman.com). Sampling time was always 24 h beginning at midnight. The filters, pre-conditioned for 2 days in a controlled room (temperature: 20±1 °C, relative humidity: 50±5%), were weighed using an analytical balance (sensitivity: 1 μg); electrostatic effects were avoided using a de-ionizing gun. The weighing procedure included several reproducibility tests and controls with certified weights. This resulted in a typical accuracy of 3–5 μg, for PM collected in the range of 300–2000 μg per filter.

The elemental composition of PM was determined by ED-XRF at the Physics Department of the Genoa University using an Oxford Instruments ED-2000 spectrometer (Ariola et al., 2006). In the ED-2000, excitation X-rays are produced by a Coolidge tube (I_{max}=1 mA, V_{max}=50 kV) with an Ag anode; the primary X-ray spectrum can be controlled by inserting filters (made of Al, Cu and Ag) between the anode and the sample. Two measuring conditions were fixed to optimize the sensitivity for groups of elements: runs with HV=15 kV, I=100 μA, no primary filter and a livetime of 1000 s, yielded the concentration of "low Z" elements (from Na to P) while the "medium-high Z" elements (from S to Pb) were measured setting HV=30 kV, I=500 μA, thin Ag primary filter and a livetime of 3000 s. X-ray spectra were fitted for 26 elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Zr, Mo, Ba, Pb) using the AXIL software

Table 1 – Sampling sites and periods

Site	Description	Sampling period			Number of daily samples		
		PM10	PM2.5	PM1	PM10	PM2.5	PM1
Brignole	Urban traffic	01/05/02→31/6/04			130		
Multedo	Heavy traffic	02/12/04→20/07/05	11/06/05→04/07/05	11/02/04→04/04/05	73	38	53
Cornigliano	Industrial	15/07/04→20/07/05	21/05/05→02/07/05	17/03/05→18/05/05	186	24	61
C.so Firenze	Urban background	17/10/03→11/06/04		21/12/03→21/09/04	92		124

Positions are indicated in Fig. 1.

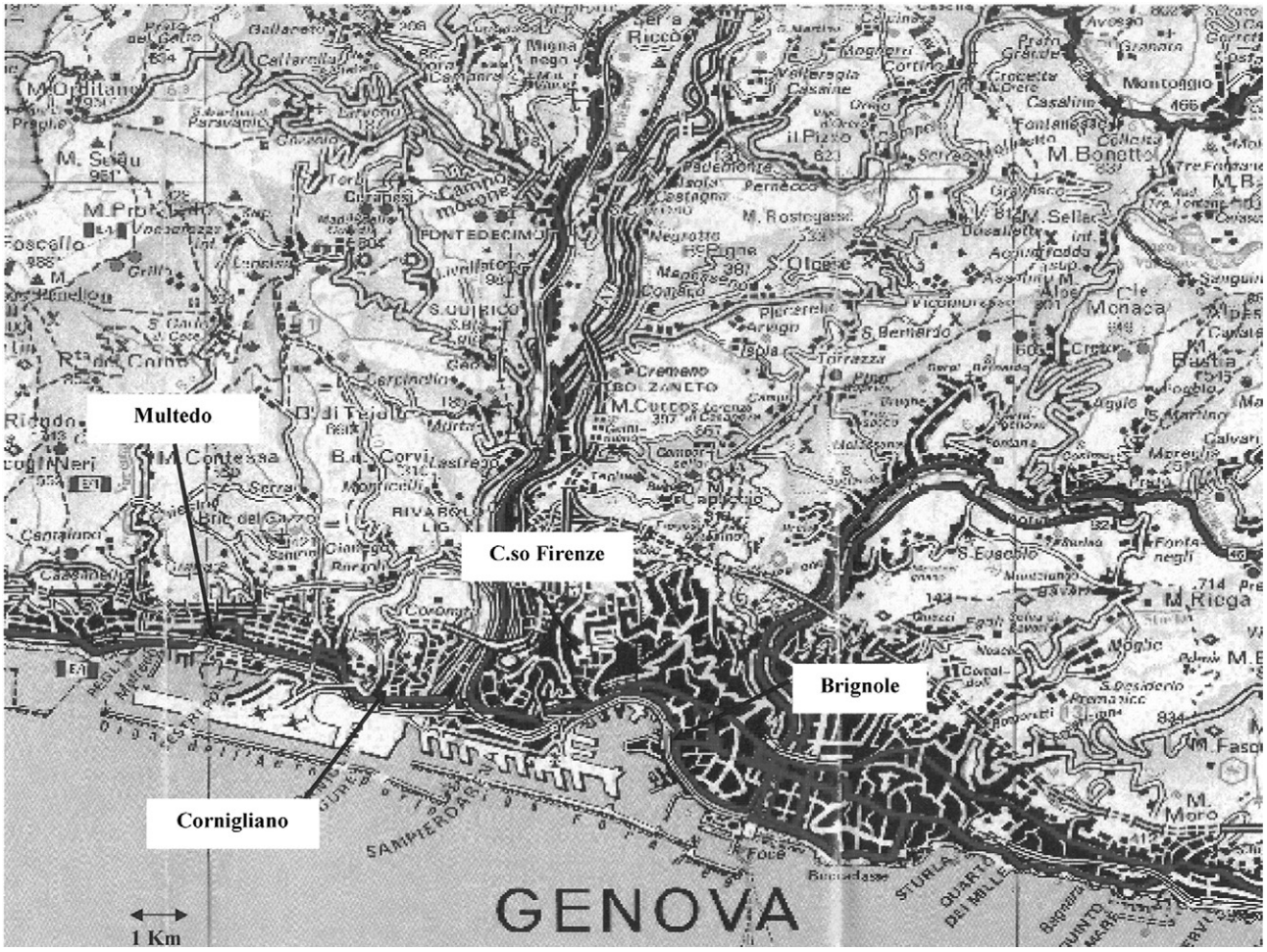

Fig. 1 – Map of the urban area of Genoa with sampling sites positions.

package (Van Espen et al., 1977). The elemental thickness [μg cm^{-2}] was obtained by comparing the filter yields with a sensitivity curve measured in the same geometry on a set of thin standards certified to within 5% (Micromatter Inc.) and converted to elemental concentration (μg m^{-3}) after accounting for the sampled air volume. Since the concentrations are obtained by direct comparison with thin standards in single grains a few μm in size the quantity of the lightest elements, like Na, Mg, Al and Si, can be somewhat underestimated due to X-ray self absorption. A check of the overall accuracy of our quantitative analysis was made by analyzing the SRM NIST 2783 standard (PM2.5 on Nuclepore polycarbonate membrane). The XRF analysis reproduced the SRM composition within experimental uncertainties except for Na, Mg, Al and Si, which were underestimated. In PM2.5 filters, Na, Mg, Al and Si concentration values obtained by XRF were therefore corrected using multiplicative factors of 1.3, 1.25, 1.2 and 1.1, respectively. In PM10 samples, we corrected the Na, Mg, Al and Si concentrations using multiplicative factors equal to 1.5, 1.4, 1.3 and 1.2, respectively, as estimated in previous works (D'Alessandro et al., 2003; Lucarelli et al., 2004). We did not apply any correction to PM1 elemental concentration values. Minimum Detection Limits (MDL) ranged from 1 to 10 ng m^{-3}. The uncertainty on measured values was on average 10% but increased to 30% for elements with low concentration (lower than 50 ng m^{-3}) and for those subject to the self absorption correction (Na and Mg).

PMF was applied to the data sets of elemental concentrations in the PM10, PM2.5 and PM1 size fractions corresponding to the sampling periods and sites quoted in Table 1. The PMF methodology has been described in detail by its developers (Paatero, 1997) and has been adopted in several studies for receptor modelling of airborne PM and for the assessment of particle source contributions (Kim et al., 2001; Liu et al., 2003; Ramadan et al., 2003; Qin et al., 2006). The concentrations values and their associated uncertainties were here treated according to the methodology suggested by Polissar (Polissar et al., 1998). To reduce the influence of extreme values on the PMF solution, the robust mode was used. The determination of the optimal solution was performed following Lee (Lee et al., 1999) and the PMF diagnostics therein described. It is worth noting that PMF is a descriptive model and there is no objective criterion to choose the best solution (Paatero et al., 2002). In this work the final solutions were determined by choosing those which were more stable with respect to different input options and those with the most physically meaningful profiles. Once the major sources of ambient PM10, PM2.5 and PM1 were identified, their apportionment was obtained by including PM mass concentration as an independent variable in the PMF analysis (Qin et al., 2006). In this

case, the PM mass data were down-weighted in the analysis by setting the uncertainties to 5 times their actual value. Technical details on the PMF analysis as well as whole daily data set considered in this work are provided elsewhere (Mazzei, 2007).

3. Results and discussion

3.1. *PM concentration and elemental composition*

A comparison of the PM compositions measured at the sampling sites listed in Table 1 is shown in Fig. 2: only elements exceeding the MDL in at least 50% of the samples are reported. Among the elements detected by XRF, sulphur is often the most abundant: this holds for all size fractions but it is particularly evident in PM1. The same evidence was obtained in a coordinated campaign, specifically devoted to the study of PM1, conducted in three Italian towns in 2004 (Vecchi et al., 2008). The elemental composition looks similar at all sites with two exceptions: 1) particularly high Fe concentration values can be observed in Cornigliano, where a steel smelter plant was operating (at this site only, Fe has a higher concentration than S); 2) Multedo, the only site where Ba and Mo, tracers of traffic (De Miguel et al., 1997), could be observed

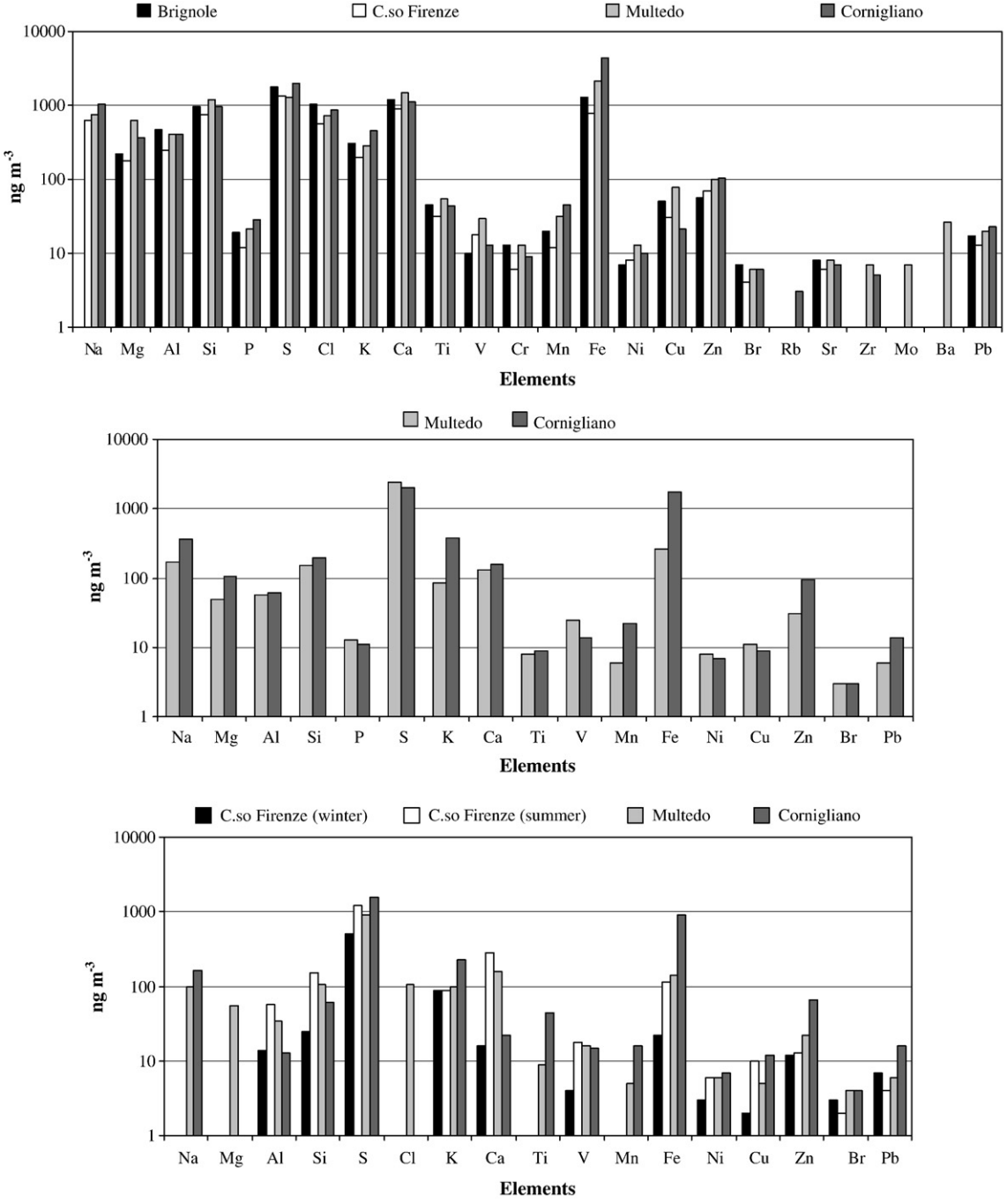

Fig. 2 – Average PM composition measured by XRF on PM10 (top), PM2.5 (middle) and PM1 (bottom) samples in the sites quoted in Table 1.

together with high values of Cu and Zn. A discussion on the air quality in town is outside the scope of this work, but in three of the four sites the PM concentrations exceeded the present and future indicative limits for PM10 and PM2.5 (see E.U. Directive 1999/30/EC and a draft of a new E.U. Directive on ambient air quality which will include limits for PM2.5), and therefore a reliable source apportionment method may become a particularly useful tool.

3.2. *Source apportionment*

Source apportionments obtained by PMF are listed in Table 2. The source profiles measured at each site are provided elsewhere (Mazzei, 2007). Measured species do not include light elements and chemical compounds (ions, organic and elemental carbon). This could possibly result in an underestimation of the impact of some sources, mainly those of anthropogenic origin. Furthermore, the PM2.5 data set is limited (see Table 1) and the number of samples collected at each site is smaller than what is considered the threshold for extracting solid results (Henry et al., 1984). Nevertheless, we consider PM2.5 in this paper, which should be taken with some caution.

Data were best modelled by extracting five sources, except in Cornigliano where six sources were needed. Some sources were identified at all sites, and according to their characteristic tracers we have called them,: "Soil" (Al and Si), "Sea" (Na, Cl and Br), "Traffic" (Cu, Zn and Pb), "Heavy Oil Combustion" (V, Ni) and "Secondary" (S). Sea was always resolved in the PM10 fraction but only at some sites in the PM2.5 and PM1 fractions. In Cornigliano, PMF did not separate the contribution of secondaries and oil combustion in PM10; for PM2.5 and PM1 the separation between the two sources was also poor. Moreover, at the same site, PMF yielded two other sources that were not resolved elsewhere: "Blast Furnace", traced by high loadings of Fe and Mn, and "Zn–Pb", probably related to other plants of the steel smelter. PM1 data collected in C.so Firenze are split into winter and summer data sets (Table 2) with some seasonal effects discussed. Specific results are presented, focusing on each detected source:

Sea: in a coastal town like Genoa, the presence of marine-related aerosols in the atmosphere is, of course, expected; however our results show significant differences from marine aerosol profiles provided by the literature. We comment here only on the PM10 data. The average Na/Cl ratio was very stable at all sites (0.9±0.4, 1.0±0.3, 0.8±0.2, in C.so Firenze, Cornigliano and Multedo, respectively); the quoted uncertainties include the correction for self-attenuation of Na X-rays. Our values are slightly different from the reference value (~0.6) (Seinfeld and Pandis, 1998). This could be due to Cl evaporation in the atmosphere. It is well known that the Cl concentration can diminish through reactions between the marine aerosol and nitric acid (Seinfeld, 1986), sulphuric acid (Singh, 1995) and SO_2 (Sievering et al., 1991). Recently, the life-time of Cl particulate in the Genoa atmosphere has been estimated to be about 1–2 h (Marenco et al., 2007). The sea profiles (Mazzei, 2007) contain sizeable concentrations of other elements (Al, Si, S and Fe) which are not typical of sea-spray aerosols. An enrichment of the sea profile with urban particulate matter is not surprising since air masses coming from the sea pass over the city before reaching the sampling sites. To quantify the impact of urban pollutants in the marine aerosol, we can compare the PMF apportionment with a simple calculation based on the measured Na. The Na concentration in the profile of the other sources is small (mostly compatible with zero). Furthermore, previous tests have shown that all the Na in PM collected in Genoa is basically in soluble form (Mazzei and Prati, 2006). Therefore we assume that all the Na comes from marine aerosol and we calculated the contribution of this source to PM10. In case of a non-polluted profile, according to Cheng et al. (2005):

$$[\text{sea}]_{\text{PM10}} = 2.54[\text{Na}] \quad (1)$$

where the square brackets denote the mass concentration and [Na] is the whole measured Na concentration. In Fig. 3, a comparison between the results obtained by the two methods is shown. In C.so Firenze and Multedo the PMF results are 86% and 80% greater, respectively, than the estimate given by Eq. (1), and the difference can almost be ascribed completely to secondary contamination. In Cornigliano the situation is different, since the PMF-based apportionment was about 2.6 times higher than the estimate given by Eq. (1) (Fig. 3). Secondary aerosol is again present, but it is very likely that extra

Table 2 – Average PM apportionment in each sampling site and size fraction

Site	Fraction	Sea	Soil	Secondary	Heavy oil combustion	Traffic	Blast furnace	Zn–Pb	PM measured
Brignole	PM10	4100±900	4600±900	12,800±2300	9700±1800	9600±1300	–	–	41,300±15,100
C.so Firenze	PM10	3000±500	4500±400	8800±1100	3200±600	5300±800	–	–	25,000±8200
Cornigliano	PM10	7000±400	3300±400	15,200±500[a]	–	6200±400	3800±400	5600±400	41,700±17,500
Multedo	PM10	3500±700	12,600±1400	5600±1500	3600±900	13,000±1900	–	–	38,800±15,500
Cornigliano	PM2.5	–	3200±200	1400±200	7600±600	3200±400	3000±300	800±200	19,000±10,300
Multedo	PM2.5	1700±500	2000±400	10,000±1200	2700±500	4700±900	–	–	20,600±6600
C.so Firenze (w)	PM1	–	1000±500	4500±1200	2000±600	1500±600	–	–	9700±4900
C.so Firenze (s)	PM1	–	4300±700	5500±1200	5000±1000	2000±6000	–	–	17,900±7700
Cornigliano	PM1	–	1300±600	2000±800	10,200±1300	1500±700	1300±700	–	17,500±8300
Multedo	PM1	1100±500	2700±600	8800±1300	2300±800	2100±700	–	–	17,600±5700

In the last column the average±standard deviation of the measured concentration. PM1 values measured in C.so Firenze are split between winter (w) and summer (s). All values are given in ng m^{-3}.

[a] In Cornigliano, PM10 data, the "secondary" and "heavy oil combustion" could not be resolved by PMF and both contributions are here summed in a unique source.

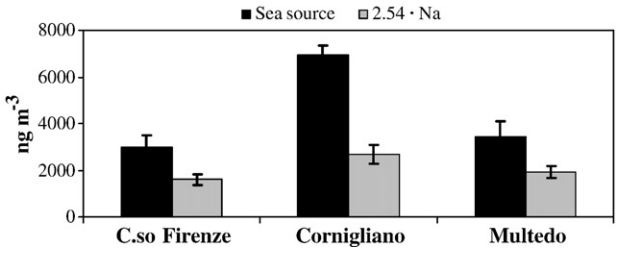

Fig. 3 – Contribution (ng m^{-3}) of marine aerosol obtained by PMF analysis (black) and by Eq. (1) (gray).

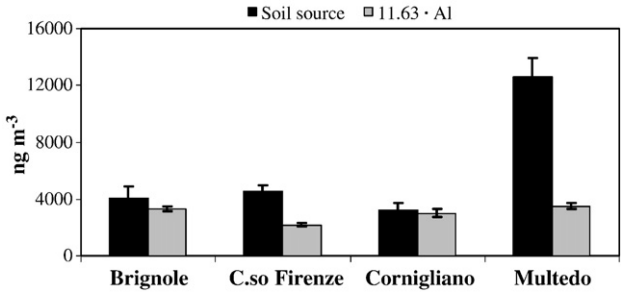

Fig. 4 – Contribution (ng m^{-3}) of soil dust obtained by PMF analysis, (black), and by Eq. (2) (gray).

contamination produced by the local steel plant is responsible for this large discrepancy. Indeed, when the wind transports marine aerosol to the sampling site, it blows from the south and passes over the industrial area (Fig. 1). The particulate matter emitted by the smelter plant, located at the seashore, is transported inland along with sea-spray particles, thus increasing the apparent "marine" aerosol contribution to PM10. Actually, simultaneous peaks can be observed in the concentration time series of Na and Fe. According to this hypothesis and assuming that the average of the PMF results in Multedo and C.so Firenze could represent the "coastal sea" (i.e., a sea profile with a pollution typical of the area, averaging about 3 μg m^{-3}), we calculated that about 4 μg m^{-3} of the 6.9 μg m^{-3} assigned by PMF to sea aerosol in Cornigliano, were actually due to steel smelter emissions.

Soil: it is traced by major crustal elements like Al, Si, Ti, Ca, Fe and Sr. Also in this case, PMF profiles reveal "interferences" with other sources (Mazzei, 2007). In general, a high concentration of Ca and Fe is found when compared with literature values (Mason, 1966). Actually, in Multedo, an enrichment in Mg and Ca was previously observed and considered with respect to a nearby quarry of magnesic lime (Formenti et al., 1997). This site is also located near a road with intense and heavy traffic, where the soil profile becomes enriched in elements (like Fe) originating from the erosion of the asphalt cement layer (De Miguel et al., 1997). On the hand, in Cornigliano, the steel smelter produces large amounts of Fe (up to 30 μg m^{-3}, daily average) and PMF tends to associate this element completely with the "blast furnace" source, reducing the Fe content in the "soil" factor to practically zero. The fraction of PM10 associated with soil by PMF was compared, according to literature (Ohta and Okita, 1990), with a simple estimate based on Al concentration:

$$[\text{Soil dust}]_{PM10} = 11.63[\text{Al}]_{PMF} \quad (2)$$

where the square brackets denote, in this case, concentration reconstructed by PMF. Indeed, it should be noted that Al could also be produced by other sources, in particular by Genoa's coal fired power plant located in the harbour area (US EPA, 2004) or by the wash-out of the alumina coat on the surface of catalytic converters of cars (Salma and Maenhaut, 2006). We prefer Eq. (2) instead of the more common evaluation based on the concentration of major crustal elements (Mason, 1966), since most of these evaluations may be strongly influenced by other sources. The results are summarized in Fig. 4: in C.so Firenze and, in particular, in Multedo, the fraction of PM10 apportioned by PMF to soil dust is higher than that corresponding to a "natural' soil, very likely due to the contribution of traffic and of the lime quarry to the concentration of crustal elements. In Brignole and Cornigliano the two approaches are in agreement even though the "soil" profile of Cornigliano is depleted in Fe (see above). In PM2.5 a contamination of the "soil" profile is also clear, in particular in Multedo where the profile shows a S to Si concentration ratio of about 1. The contribution of soil dust to PM2.5 ranges between 10% and 17%. Similar values have been found in other works (Qin et al., 2006). In PM1 the soil dust profile is quite different from literature values (Mason, 1966), with the exception of the summer data set of C.so Firenze (Mazzei, 2007). Actually, during this period maintenance works was performed on the road surface around the sampling site and the fraction of PM1 apportioned by PMF to soil dust is particularly high (about 4 μg m^3, Table 2). We conclude that the urban soil in Genoa can only partially be considered a natural source, because the apportionment based on crustal elements includes, in some cases, large fractions of PM with a different origin.

Traffic: in this case a comparison with a fixed profile is not possible, as this source is actually a mixture of several contributions. Nevertheless, the profiles obtained at the four sites can be compared and the results for tracers of traffic are given in Table 3. The Cu:Pb concentration ratio, based on the fraction of these elements attributed by PMF to traffic, is fairly constant at the four sites; the same holds for the Cu:Zn concentration ratio but with a clear discrepancy in Cornigliano. Actually, the steel smelter plant produces relatively high Zn concentration

Table 3 – Tracer concentration ratios (average ± uncertainty) in the profiles of the sources named as "traffic" and "heavy oil combustion"; "n.c" stands for "not calculated"

Size fraction	Tracers ratio	Brignole	Cornigliano	C.so Firenze	Multedo
PM10	Cu:Pb	4.0±0.7	5.0±0.7	2.9±0.6	3.7±0.4
PM2.5	Cu:Pb	–	2.3±0.8	–	3.0±0.8
PM1	Cu:Pb	–	0.5±0.3	0.5±0.1	0.5±0.3
PM10	Cu:Zn	1.0±0.2	3.3±1.2	0.9±0.2	1.1±0.1
PM2.5	Cu:Zn	–	0.3±0.1	–	0.3±0.1
PM1	Cu:Zn	–	0.11±0.06	n.c.	0.07±0.02
PM10	V:Ni	3.0±0.9	1.0±0.4	3.0±0.7	3.8±1.1
PM2.5	V:Ni	–	3.3±0.6	–	3.5±0.8
PM1	V:Ni	–	2.0±0.6	3.1±0.9	3.7±1.2

(Prati et al., 2000) and, very likely, the PMF analysis overloads Zn for the smelter plant (thus "depleting" Zn in traffic). Taking into account the peculiarity of Cornigliano, we averaged all the other values and concluded that in PM10, traffic emissions in Genoa can be identified by the concentration ratios: Cu:Pb = 3.9±0.6 and Cu:Zn = 1.0±0.2. Significative concentrations of crustal elements are also attributed by PMF to traffic probably due to soil dust deposited on the road surface and to road erosion and the subsequent emission and re-suspension. In Multedo, the site with the highest contribution of traffic to PM10, Ba and Mo concentrations were detected with Cu:Ba and Cu:Mo concentration ratios of about 3 and 10, respectively. In PM2.5, the concentration ratios between Cu and Zn and Cu and Pb are again fairly constant at all sites (see Table 3) but with values different from those found for PM10; averages are: Cu:Pb = 2.6±0.8 and Cu:Zn = 0.3±0.1. Traffic profiles in PM2.5, as in PM10, show significant concentrations of crustal elements. In PM1, the source identified as "traffic" gives a constant behaviour only for the concentration ratio Cu:Pb (town average = 0.5±0.2, see Table 3), the Cu:Zn concentration ratio has a near constant value in Cornigliano and Multedo (Table 3) but it is highly variable in C.so Firenze. The present data do not allow the extraction of a reliable town average.

Values of concentration ratios between other traffic tracers (Cu and Sb, in particular) have been reported in previous works (Salma and Maenhaut, 2006) and together with the present results they contribute to a firm identification of the traffic contribution to PM concentration in urban environments.

Heavy oil combustion: we followed the same approach described for the traffic source. The V to Ni concentration ratio calculated by PMF is similar at three of the four sites (Table 3) and it is also fairly constant for the three size fractions. This can be expected, since the PM1:PM2.5 and PM2.5:PM10 ratios are close to 1 for combustion products (Ariola et al., 2006). In Cornigliano, the "Secondary" and "Heavy oil combustion" turned out to be mixed in the same source, and V and Ni concentrations were distributed by PMF in several sources almost homogeneously. Neglecting the Cornigliano PM10 data, we conclude that heavy oil combustion is identified by the concentration ratio V:Ni = 3.2±0.8 in all PM fractions; a similar value has been found in other work (Hedberg et al., 2005). Concentration ratios V:Ni = 3.5–4, have been measured very recently in tests of different ship engines and fuels by sampling directly at the exhausts of the auxiliary engine used by vessels in harbours (Nigam et al., 2006). A particularly high contribution of heavy oil combustion to PM1 (about 5 $\mu g\ m^{-3}$) was found in the summer data set of C.so Firenze (Table 2). This could be related with the notable increase of the traffic of passenger ships in the harbour during the holiday period. Significant stationary sources (e.g. power plants) that burn residual oil are not present in the urban area of Genoa, so it can be supposed that the harbour activity is the dominant source of heavy oil combustion.

Secondary compounds: Sulphur is mainly attributed to this source, although a significant concentration is also present in the Heavy Oil Combustion profiles (Mazzei, 2007). The fraction of PM apportioned by "Secondary" is dominant almost everywhere (with the exception of PM10 in Multedo, and PM2.5 and PM1 in Cornigliano where the PMF separation of "Heavy Oil" and "Secondary" does not look completely firm). The fraction of PM attributed to "Secondary" could not be explained assuming $(NH_4)_2SO_4$ as the unique secondary compound of S. In fact, at all sites the ratio of Secondary, as determined by PMF, to S concentration is much higher than 4.1, even considering the total measured S. This probably indicates that part of S and of the secondary PM was actually associated with nitrates and/or organic compounds. A PM2.5 nitrates profile showing a non-negligible S content has been recently reported (Qin et al., 2006).

Industry: In Cornigliano only, PMF resolved two sources, named as "Blast Furnace" and "Zn–Pb" (Table 2). These are very likely related to the steel smelter activity. The impact of these local sources on air quality has been discussed in other works (Prati et al., 2000; Mazzei, 2007). We do not treat this topic further, as the present paper is focused on the comparison of sources identified at all sites.

4. Conclusions

In the framework of a long-lasting campaign to characterize the PM sources in the city of Genoa, about 1600 daily elemental concentration values in PM10, PM2.5 and PM1 at four sampling sites were measured and analyzed. They formed the data base for source apportionment performed by PMF. For the cases of sources aligned with the wind direction, of elements emitted by multiple sources (e.g. Fe and S) and of the presence of peculiar and dominant sources (as in the industrial district of Cornigliano) the data yielded particularities in the source apportionment. PMF applied produced stable results (profiles and apportionment) when applied to daily data sets and yielded significant information on anthropogenic sources, even though the information collected at each site (elemental concentrations detectable by XRF only with no data on organic compounds, ions and elemental carbon) was somewhat limited. Town averages for the concentration ratios of tracers of traffic and oil combustion were deduced. The approach followed in this study, in particular the use of data collected at different sites of the same urban area, could be used in other cases to disentangle the possible mixing of sources with similar emission profiles, and to resolve the correct fraction of PM associated with natural sources.

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